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(54) Title: FLUORINATION CATALYST AND PROCESS

(57) Abstract

A chromium-free fluorination catalyst comprising an activity-promoting amount of zinc supported on an alumina, halogenated alumina or aluminium oxyhalide support and use of the catalyst for the production of fluorinated hydrocarbons by reacting a hydrocarbon or a halogenated hydrocarbon with hydrogen fluoride in the vapour phase in the presence of the catalyst.

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FLUORINATION CATALYST AND PROCESS

This invention relates to an improved fluorination catalyst and to a process for the production of fluorinated hydrocarbons by the catalysed reaction of hydrocarbons and halogenated hydrocarbons with hydrogen fluoride. The 5 invention relates in particular to a promoted alumina, halogenated alumina or aluminium oxyhalide catalyst and relates in a particular embodiment to a process for the production of 1,1,1,2-tetrafluoroethane by the catalysed reaction of 1-chloro-2,2,2-tetrafluoroethane with hydrogen 10 fluoride.

The production of fluorinated hydrocarbons, which may also contain halogen atoms other than fluorine, by the catalysed vapour-phase fluorination of hydrocarbons and halogenated hydrocarbons with hydrogen fluoride is well 15 known and numerous catalysts have been proposed for use in such process. Catalysts comprising or based on chromium and in particular chromia are frequently employed in the known processes. Furthermore, it has also been proposed to promote the activity of these chromium containing catalysts by the 20 incorporation in the catalyst of an activity promoting amount of certain metals, for example zinc, nickel, cobalt and manganese.

Thus, for example chromia or a halogenated chromia may be used in the vapour-phase reaction of trichloroethylene 25 with hydrogen fluoride to produce 1-chloro-2,2,2-trifluoroethane as described in GB Patent 1,307,224 and in the vapour-phase reaction of 1-chloro-2,2,2-trifluoroethane with hydrogen fluoride to produce 1,1,1,2-tetrafluoroethane as described in GB Patent 30 1,589,924. The same catalyst may be used for the fluorination of chlorodifluoroethylene to 1-chloro-2,2,2-trifluoroethane. GB Patent 1,589,924 describes the removal of chlorodifluoroethylene impurity 35 from 1,1,1,2-tetrafluoroethane by reacting the impurity with hydrogen fluoride.

Catalysts may also comprise chromium upon a metal oxide, halogenated oxide or oxyfluoride support, for example alumina or magnesia, and during the fluorination process in which the catalyst is employed, the chromium may be converted to chromia, halogenated chromia or a chromium oxyfluoride. It has now been found that whilst in the absence of chromium, these supports show very little catalytic activity alone, some supports may be given a significant activity by the incorporation of an activity promoting amount of zinc.

According to the present invention there is provided a chromium-free fluorination catalyst comprising an activity-promoting amount of zinc or a compound of zinc supported on an alumina, halogenated alumina or aluminium oxyhalide support.

According to the invention also there is provided a process for the production of fluorinated hydrocarbons which comprises reacting a hydrocarbon or a halogenated hydrocarbon with hydrogen fluoride in the vapour phase in the presence of a fluorination catalyst as defined in the immediately preceding paragraph.

The amount of zinc incorporated in the catalyst is such as to result in promotion of the activity of the alumina, halogenated alumina or aluminium oxyhalide into which the zinc promoter is incorporated. The amount is important since the incorporation of too much of the zinc promoter may result in a decrease rather than an increase in catalyst activity when compared to the activity of the catalyst when the optimum amount of zinc promoter is incorporated and it is only when the zinc promoter is present in the correct amount that optimum activity promotion occurs.

The amount of zinc promoter incorporated in the catalyst to achieve significant activity promotion will depend upon the basic support employed, in particular the surface area of the support and upon the method used to

5 prepare the improved catalyst. However, for any particular support and catalyst preparation method, the optimum amount of zinc promoter is readily determined by simple routine experiment. Overall, the amount of zinc will usually be in the range from about 0.5% to about 30%, and preferably from about 1.5% to about 25% by weight of the catalyst.

10 The optimum amount of zinc incorporated depends on the surface area of the catalyst, in particular the "working" surface area of the catalyst". The working surface area of the catalyst is the surface area of the catalyst measured after catalyst preparation and pre-treatment with hydrogen fluoride (as described hereafter) or, if the catalyst is not pre-treated with hydrogen fluoride, after the catalyst has been employed in a vapour phase fluorination reaction in which hydrogen fluoride is employed. The working surface area of the catalyst may be in the range from about 10 to about 100m²/g, typically from about 10 to about 50 m²/g. Where the catalyst is prepared from alumina, alumina with a surface area of from about 50m²/g to about 400m²/g, gives a catalyst after preparation and pre-treatment with a working surface area in the defined range. The catalyst may be prepared from starting aluminas having a surface area from about 50m²/g to about 250m²/g and preferably from about 150m²/g to about 250m²/g.

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20 As stated above, the amount of promoter incorporated in the catalyst also depends upon the catalyst preparation employed. The effective part of the catalyst is believed to be the surface of the support containing zinc promoter cations located in an alumina, halogenated alumina or aluminium oxyhalide lattice and it is the amount of such surface zinc promoter which determines the activity of the catalyst. The activity-promoting effect of the zinc promoter per unit weight of the zinc promoter is generally higher for catalysts made by impregnation than for catalysts made by

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other methods and containing the zinc promoter in non-surface locations.

By way of example, in the case of zinc incorporated by impregnation on an alumina support, the alumina used to 5 prepare the catalyst having a surface area of 180m²/g, optimum activity promotion results when the amount of zinc is within the range of about 0.5% by weight to about 10% by weight of the catalyst, preferably within the range from about 0.5% to about 6%, more preferably in the range from 10 about 1.5% to about 4% and especially in the range from about 1.5% to about 3.5%; less than 0.5% by weight of zinc may be insufficient to result in significant promotion of catalyst activity whilst more than about 8% by weight of zinc may result in no significant increase in catalyst 15 activity when compared to the activity promotion provided by the above optimum ranges of zinc. By contrast, in the case of a catalyst prepared by co-precipitation and in which significant amounts of zinc are incorporated in non-surface locations, the amount of zinc may be within the range from about 3% to about 30% by weight of the catalyst, preferably from about 4% to about 25% by weight of the catalyst, especially from about 5% to about 15% by weight of the 20 catalyst.

The zinc promoter may be incorporated in the catalyst 25 in the form of a compound, for example a halide, oxyhalide, oxide or hydroxide depending at least to some extent upon the catalyst preparation technique employed. In the case where catalyst preparation is by impregnation of aluminium oxide, halogenated aluminium oxide or aluminium oxyhalide support, the compound is preferably a water-soluble salt, 30 for example a halide, nitrate or acetate, and is employed as its aqueous solution. The hydroxides of the promoter and aluminium may be co-precipitated and then converted to the oxides to prepare the catalyst. Mixing and milling of insoluble zinc compounds with the basic catalyst provides a 35

further method of preparing the catalyst. A method for making catalysts based on aluminium oxyhalide comprises adding a compound of the promoter to hydrated aluminium fluoride and calcining the mixture.

5 Any of the aforementioned methods or indeed other methods may be employed for the preparation of the zinc promoted catalysts of the present invention.

10 The fluorination catalyst will usually be subjected to a prefluorination treatment with hydrogen fluoride and optionally an inert diluent prior to use in the catalysis of fluorination reactions. A typical pretreatment comprises heating the catalyst at 250°C to 450°C in contact with hydrogen fluoride, or a mixture of hydrogen fluoride and air. Consequently the working catalyst is believed to be at least partially zinc fluoride supported on fluorinated 15 alumina or aluminium oxyfluoride.

20 The catalyst may be used in the form of pellets or granules of appropriate size for use in a fixed bed or a fluidised bed. It may be regenerated or reactivated periodically by heating in air at a temperature of from about 300°C to about 500°C. Air may be used as a mixture with an inert gas such as nitrogen or with hydrogen fluoride which emerges hot from the catalyst treatment process and may be used directly in vapour phase fluorination processes.

25 The activity of the base (unpromoted) alumina, halogenated alumina or aluminium oxyhalide catalyst is enhanced by the incorporation of the promoter. The selectivity of the reaction catalysed by the catalyst towards the production of 1,1,1,2-tetrafluoroethane from 30 1-chloro-2,2,2-trifluoroethane and hydrogen fluoride may be at least as high as that using the corresponding unpromoted catalysts, typically in excess of 85%.

If desired, the catalyst may contain one or more metals other than zinc, for example nickel, copper, manganese, cobalt, and iron, and in particular iron, cobalt and copper

since the presence of one or more of these metals may enhance the extent to which catalyst activity may be restored by regeneration of the catalyst. At the particularly preferred loadings of zinc, we generally prefer to employ only zinc or at least predominantly zinc, with only small amounts, say less than 2.0% by weight, preferably less than 1.5% by weight and especially less than 1.0% by weight of other metals present. Where however, the catalyst comprises a relatively high loading of zinc, say for example in the case of a catalyst prepared by impregnation, greater than about 3%, preferably greater than about 4% and especially greater than about 5% by weight zinc, we prefer to incorporate small amounts of iron, in particular, in addition to zinc, for example to incorporate an amount of iron in the range from about 0.1% by weight to about 2% by weight, preferably from about 0.1% by weight to about 1.5% by weight and more preferably from about 0.5% to about 1.5% by weight of the catalyst. The ratio (wt% based on the weight of the catalyst) of zinc to iron is preferably in the range from about 80:1 to about 2:1, more preferably in the range from about 16:1 to about 2:1. This ratio is preferred irrespective of the absolute amounts of zinc and iron in the catalyst.

Thus, although the absolute amounts of zinc and iron may be higher, for example at least 6%, preferably at least 10% zinc by weight of the catalyst, and an amount of iron in the range from about 0.2% to about 12%, preferably from about 0.4% to about 4.5% by weight of the catalyst, in respect of catalysts prepared by methods, for example co-precipitation, which lead to significant amounts of zinc and iron being incorporated in the catalyst in non-surface locations, the relative amounts of zinc and iron (wt% based on the weight of the catalyst) is also preferably within the ranges given above.

A further feature of the invention resides in use of the promoted catalyst in fluorination processes comprising reaction of a hydrocarbon or halogenated hydrocarbon with hydrogen fluoride in the vapour-phase.

5 Alkenes (unsaturated hydrocarbons) and in particular halogenated alkenes, for example trichloroethylene or halogenated alkanes of 1-4C atoms preferably containing at least one chlorine atom may be fluorinated and examples of specific fluorinations which may be effected are the production of 1,1,1,2-tetrafluoroethane from
10 1-chloro-2,2,2-trifluoroethane, the production of 1-chloro-2,2,2-trifluoroethane from trichloroethylene and the conversion of 1-chloro-2,2-difluoroethylene to 1-chloro-2,2,2-trifluoroethane. Examples of other
15 fluorination reactions in which the catalyst is useful are the reaction of perchloroethylene with hydrogen fluoride in vapour phase to produce dichlorotrifluoroethane (123), chlorotetrafluoroethane (124) and/or pentafluoroethane (125), and the reaction of perchloroethylene with chlorine and hydrogen fluoride in vapour phase to produce
20 trichlorotrifluoroethane (113), dichlorotetrafluoroethane (114/114a) and/or chloropentafluorothane (115).

The fluorination conditions employed may be those known to be useable when employing chromia or halogenated chromia as the catalyst, for example atmospheric or superatmospheric pressure, hydrogen fluoride and temperatures in the range of 180°C to about 500°C depending upon the particular fluorination reaction being carried out.

However, the increased activity of the promoted catalyst permits reactions to be carried out without loss of efficiency at significantly lower temperatures than those required to achieve similar activity using the unpromoted alumina. For example whilst yields of only 0.5% 30 1,1,1,2-tetrafluoroethane from 1-chloro-2,2,2-trifluoroethane may be achieved at
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atmospheric pressure when using the relatively high temperature of 360°C or above when using unpromoted alumina, a lower temperature of say 280°C is sufficient to achieve greater reaction efficiency using a zinc-promoted alumina.

5 Alternatively, if the temperature is the same, say 300°C, a shorter contact time is required using the promoted catalyst.

A preferred embodiment of the process of the invention resides in a process for the preparation of 1,1,1,2-tetrafluoroethane which comprises reacting 1-chloro-2,2,2-trifluoroethane with hydrogen fluoride in the vapour phase in the presence of the promoted catalyst of the invention. This process may be carried out under atmospheric or superatmospheric pressure at a temperature of from about 280°C to 500°C.

15 The process may be one stage of a two or three-stage process, for example it may be the second stage of a process for the production of 1,1,1,2-tetrafluoroethane from trichloroethylene, the first stage being the vapour-phase fluorination of trichloroethylene with hydrogen fluoride in the presence of a fluorination catalyst to produce 20 1-chloro-2,2,2-trifluoroethane. The promoted catalyst of the invention may be used in the first stage as well as in the second stage of this two-stage process. Typical reaction conditions for the the first stage are atmospheric or 25 superatmospheric pressure and a temperature in the range of about 180°C to about 400°C.

The production of 1,1,1,2-tetrafluoroethane from 30 1-chloro-2,2,2-trifluoroethane results in a product stream containing the toxic impurity 1-chloro-2,2,-difluoroethylene. This impurity can be removed by reacting it with hydrogen fluoride in the vapour phase in the presence of a fluorination catalyst at a temperature below about 270°C, for example 150°C to 270°C. The promoted catalyst of the invention may be employed in this reaction.

thus providing a three-stage process for the preparation of 1,1,1,2-tetrafluoroethane essentially free from 1-chloro-2,2-difluoroethylene from trichloroethylene using the promoted catalyst in one or more of each of the three reaction stages.

A particularly preferred embodiment of the above-described two-stage process for preparing 1,1,1,2-tetrafluoroethane from trichloroethylene comprises the steps of:

(A) contacting a mixture of 1-chloro-2,2,2-trifluoroethane and hydrogen fluoride with a fluorination catalyst at a temperature in the range from about 280 to about 450°C in a first reaction zone to form a product containing 1,1,1,2-tetrafluoroethane and hydrogen chloride together with unreacted starting materials,

(B) passing product of step A together with trichloroethylene to a second reaction zone containing a fluorination catalyst at a temperature in the range from about 180°C to about 400°C but lower than the temperature in step A to form a product containing 1-chloro-2,2,2-trifluoroethane, 1,1,1,2-tetrafluoroethane, hydrogen chloride and unreacted trichloroethylene and hydrogen fluoride,

(C) treating product of step B to separate hydrogen chloride and 1,1,1,2-tetrafluoroethane from 1-chloro-2,2,2-trifluoroethane, unreacted hydrogen fluoride and unreacted trichloroethylene; and

(D) feeding 1-chloro-2,2,2-trifluoroethane obtained from step C together with hydrogen fluoride to said first reaction zone step (A), wherein a chromium-free fluorination catalyst as previously described herein is employed in at least one of steps (A) and (B).

At least the stoichiometric amount of hydrogen fluoride is usually employed in step A of the preferred embodiment.

Typical amounts include from 1 to 10 moles, and preferably from 1 to 6 moles, of hydrogen fluoride per mole of 1-chloro-2,2,2-trifluoroethane. Accordingly, the product of this reaction step will usually contain unreacted hydrogen fluoride in addition to 1,1,1,2-tetrafluoroethane, hydrogen chloride and by-products. Preferred reaction temperatures for this stage of the process are in the range from 325°C to 385°C with contact times of from 1 to 100 and preferably from 5 to 30 seconds at 5 to 20 bars pressure.

From 10 to 100, preferably from 15 to 60, moles of hydrogen fluoride per mole of trichloroethylene are typically employed in Step B. Again, the reaction product of this stage will normally contain unreacted hydrogen fluoride. Contact times of 1 to 100 seconds, preferably 5 to 30 seconds may be used, typically at 220-350°C and 5 to 20 bars pressure.

It is preferred that the process according to the invention, including preferred embodiments, is operated continuously. In practice, however, catalyst deactivation, necessitating periodic catalyst regeneration or reactivation may interrupt continuous operation of the process. The feeding of air to the catalyst during operation of the process may counter catalyst deactivation and reduce the frequency of process interruption for catalyst regeneration or reactivation.

The invention is illustrated but in no way limited by the following examples.

EXAMPLES 1 TO 7

4.79g of alumina (supplied by Harshaw Ltd) in the form of granules of size 0.5-1.4mm, and having a surface area of 180m²/g, was added to an aqueous solution of zinc chloride (0.21g) in distilled water (10ml) and stirred to ensure thorough wetting of the solid by the solution. The mixture

was then dried by direct heating and the resultant solid sieved to give particles of size 0.5-1.4mm of a finished catalyst comprising about 2.0% w/w zinc on alumina. The above procedure was repeated except that zinc chloride solutions of increasing concentration were employed in order to produce a range of finished catalysts with up to 6.6% w/w zinc in the finished catalyst. The fluorination activities of the zinc promoted aluminas were measured using an atmospheric pressure microreactor. Catalysts (2g) were charged to a 1/4" diameter microreactor and were conditioned in a stream of HF at 300°C for 1 hour and then heated to 350°C and further conditioned in an air/HF (ratio 1:20) stream for approximately 15hrs.

The microreactor was then fed with a mixed 1-chloro-2,2,2-trifluoroethane (133a) and HF feed using a molar feed ratio of 1.0:3.5, which gave a 2 second contact time at 300°C.

For purposes of comparison the unpromoted alumina from which the promoted aluminas were prepared was also tested.

The results of the study are presented as % yields of 1,1,1,2-tetrafluoroethane in Table 1 and demonstrate the beneficial effect of zinc addition to alumina on increasing the yield of 1,1,1,2-tetrafluoroethane (134a).

The activity of the zinc-impregnated alumina catalyst reached a peak at a zinc content in the range of about 2% to about 3% w/w.

TABLE 1

EXAMPLE	CATALYST	REACTION TEMPERATURE (°C)					
		360	350	340	330	320	
5	1	0.5%Zn-Al ₂ O ₃	6.3	4.3	1.96	-	-
	2	1.0%Zn-Al ₂ O ₃	7.5	5.5	3.27	-	-
	3	2.0%Zn-Al ₂ O ₃	20.1	17.2	11.3	-	-
	4	2.2%Zn-Al ₂ O ₃	-	16.5	11.0	7.4	4.9
10	5	3.0%Zn-Al ₂ O ₃	18.7	15.1	11.2	-	-
	6	4.4%Zn-Al ₂ O ₃	13.6	9.4	6.6	-	-
	7	6.6%Zn-Al ₂ O ₃	10.6	8.1	6.3	-	-
15	Comp	Al ₂ O ₃	0.25	0.15	0.09	-	-

EXAMPLE 8.

4.39g of alumina (supplied by Marshaw Ltd) in the form of granules of size 0.5-1.4mm, and having a surface area of 180m²/g, was added to an aqueous solution of nickel (II) chloride hexahydrate (0.41g) and zinc chloride (0.21g) in distilled water (5ml) and stirred to ensure thorough wetting of the solid by the solution. The mixture was then dried by direct heating and the resultant solid sieved to give particles, of size 0.5-1.4mm, of a finished catalyst comprising about 2.0% w/w zinc and about 2% w/w nickel on alumina.

2g of this catalyst was tested at atmospheric pressure according to the procedure of examples 1 to 7.

For purposes of comparison the activity of catalysts comprising 2% and 3.8% by weight nickel on alumina, prepared from an aqueous solution of nickel (II) chloride as described above were also measured. The atomic loading of the 3.8% nickel on alumina catalyst is the same as that of the catalyst containing 2% zinc and 2% nickel.

The results of the study are shown as % yields of 1,1,1,2-tetrafluoroethane in Table 2 and demonstrate the beneficial effect of zinc/nickel addition to alumina compared to alumina alone, but nevertheless inferior effect of zinc/nickel addition compared to zinc addition alone and the even poorer effect of nickel addition alone.

TABLE 2

EXAMPLE	CATALYST	REACTION TEMPERATURE(°C)				
		340	330	320	310	300
8	2%Zn/2%Ni-Al ₂ O ₃	6.4	5.1	3.6	2.7	1.9
Comp	2%Ni-Al ₂ O ₃	3.1	2.3	1.6	1.1	0.7
Comp	3.8%Ni-Al ₂ O ₃	2.6	1.8	1.3	0.8	0.5

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EXAMPLE 9.

4.39g of alumina (supplied by Harshaw Ltd) in the form of granules of size 0.5-1.4mm, and having a surface area of 180m²/g, was added to an aqueous solution of cobalt (II) chloride hexahydrate (0.404g) and zinc chloride (0.21g) in distilled water (5ml) and stirred to ensure thorough wetting of the solid by the solution. The mixture was then dried by direct heating and the resultant solid sieved to give particles of size 0.5-1.4mm of a finished catalyst comprising 2.0% w/w zinc and 2% w/w cobalt on alumina.

2g of this catalyst was tested at atmospheric pressure according to the procedure of examples 1 to 7.

For purposes of comparison the activity of catalysts comprising 2% and 3.8% by weight cobalt on alumina, prepared

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from an aqueous solution of cobalt (II) chloride as described above, were also measured. The atomic loading of the 3.8% cobalt on alumina catalyst is the same as that of the catalyst containing 2% zinc and 2% cobalt.

5 The results of the study are shown as % yields of 1,1,1,2-tetrafluoroethane in Table 3 and demonstrate the beneficial effect of zinc/cobalt addition to alumina compared to alumina alone, but nevertheless inferior effect of zinc/cobalt addition compared to zinc addition alone and 10 the even poorer effect of cobalt addition alone.

TABLE 3

EXAMPLE	CATALYST	REACTION TEMPERATURE(°C)				
		340	330	320	310	300
9	2%Zn/2%Co-Al ₂ O ₃	10.9	7.0	5.6	3.6	2.8
Comp	2%Co-Al ₂ O ₃	3.8	2.6	1.5	1.0	0.5
Comp	3.8%Co-Al ₂ O ₃	3.4	2.5	1.8	1.3	0.9

EXAMPLE 10.

25 4.43g of alumina (supplied by Harshaw Ltd) in the form of granules of size 0.5-1.4mm, and having a surface area of 180m²/g, was added to an aqueous solution of manganese (II) chloride tetrahydrate (0.36g) and zinc chloride (0.21g) in distilled water (5ml) and stirred to ensure thorough wetting 30 of the solid by the solution. The mixture was then dried by direct heating and the resultant solid sieved to give particles of size 0.5-1.4mm of a finished catalyst comprising 2.0% w/w zinc and 2% w/w manganese on alumina.

2g of this catalyst was tested at atmospheric pressure according to the procedure of examples 1 to 7.

For purposes of comparison the activity of catalysts comprising 2% and 3.68% by weight manganese on alumina, prepared from an aqueous solution of manganese (II) chloride as described above, were also measured. The atomic loading of the 3.68% manganese on alumina catalyst is the same as that of the catalyst containing 2% zinc and 2% manganese.

The results of the study are shown as % yields of 1,1,1,2-tetrafluoroethane in Table 4 and demonstrate the beneficial effect of zinc/manganese addition to alumina compared to alumina alone, but nevertheless inferior effect of zinc/manganese addition compared to zinc addition alone and the even poorer effect of manganese addition alone.

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TABLE 4

EXAMPLE	CATALYST	REACTION TEMPERATURE (°C)			
		340	330	320	310
10	2%Zn/2%Mn-Al ₂ O ₃	10.5	7.7	6.7	4.5
Comp	2%Mn-Al ₂ O ₃	1.0	0.7	0.4	0.3
25	3.68%Mn-Al ₂ O ₃	0.6	0.5	0.3	0.2

EXAMPLES 11 to 20.

4.30g of alumina (supplied by Harshaw Ltd) in the form of granules of size 0.5-1.4mm, and having a surface area of 180m²/g, was added to an aqueous solution of iron (III) chloride (0.07g) and zinc chloride (0.63g) in distilled water (10ml) and stirred to ensure thorough wetting of the solid by the solution. The mixture was then dried by direct heating and the resultant solid sieved to give particles, of

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size 0.5-1.4mm, of a finished catalyst comprising 6.0% w/w zinc and 0.5% w/w iron on alumina. The above procedure was repeated except that iron (III) chloride and zinc chloride solutions of different concentrations were used to give a range of finished catalysts having the zinc and iron loadings shown in Table 5.

2g of each of these catalysts were tested at atmospheric pressure according to the procedure of examples 1 to 7.

For purposes of comparison the activity of a catalyst comprising 2% by weight iron on alumina, prepared from an aqueous solution of iron (III) chloride as described above, was also measured. The atomic loading of the 6% w/w zinc and 0.5% w/w iron on alumina is equal to that of the 6.6% w/w zinc on alumina catalyst (example 7) and the activity of the catalyst of example 7 and examples 3, 5 and 6 are also shown below for the purposes of comparison.

The results of the study are shown as % yields of 1,1,1,2-tetrafluoroethane in Table 5 and demonstrate the beneficial effect of zinc/iron addition to alumina compared to the addition of iron alone or zinc alone at relatively high loadings of zinc and zinc to iron ratios of greater than 2:1.

TABLE 5

EXAMPLE	CATALYST	REACTION TEMPERATURE (°C)				
		360	350	340	330	320
11	2%Zn/1%Fe-Al ₂ O ₃	13.2	11.6	8.9	-	-
12	2%Zn/2%Fe-Al ₂ O ₃	13.9	10.5	8.5	-	-
13	3%Zn/1%Fe-Al ₂ O ₃	19.3	16.3	10.9	-	-
14	3%Zn/2%Fe-Al ₂ O ₃	16.0	12.8	9.7	7.6	-
15	3%Zn/3%Fe-Al ₂ O ₃	10.9	9.4	6.9	-	-
16	3%Zn/5%Fe-Al ₂ O ₃	9.8	8.9	6.9	-	-
17	4%Zn/1%Fe-Al ₂ O ₃	13.4	12.4	9.9	-	-
18	4%Zn/2%Fe-Al ₂ O ₃	12.2	8.9	7.7	5.9	-
19	6%Zn/0.5%Fe-Al ₂ O ₃	13.4	13.7	9.9	6.5	4.5
20	6%Zn/1.5%Fe-Al ₂ O ₃		13.4	9.4	8.5	5.4
Comp:	2%Fe-Al ₂ O ₃	1.0	0.6	-	-	-
3	2%Zn-Al ₂ O ₃	20.1	17.2	11.3	-	-
5	3%Zn-Al ₂ O ₃	18.7	15.1	11.2	-	-
6	4.4%Zn-Al ₂ O ₃	13.6	9.4	6.6	-	-
7	6.6%Zn-Al ₂ O ₃	10.6	8.1	6.3	-	-

EXAMPLES 21 to 25.

The following examples illustrate that of the metal species tested in conjunction with zinc only iron gives a more active catalyst than the 6.6% by weight zinc on alumina catalyst.

The catalysts were prepared according to the method described previously for examples 1 to 12 except that the solutions to which the alumina was added were as follows:

10 Example 21 same as example 12.

Example 22 4.07g of alumina added to an aqueous solution of 0.63g of $ZnCl_2$ and 0.3g of $CoCl_2$ hexahydrate in 10 ml of water.

15 Example 23 4.07g of alumina added to an aqueous solution of 0.63g of $ZnCl_2$ and 0.3g of $NiCl_2$ hexahydrate in 10 ml of water.

20 Example 24 4.04g of alumina added to an aqueous solution of 0.63g of $ZnCl_2$ and 0.34g of $Mn(CH_3CO_2)_2$ tetrahydrate in 10ml of water.

25 Example 25 4.17g of alumina added to an aqueous solution of 0.63g of $ZnCl_2$ and 0.2g of $CuCl_2$ dihydrate in 10 ml of water.

30 2g of each of these catalysts were tested at atmospheric pressure according to the procedure of examples 1 to 7.

35 The results of the study are shown as % yields of 1,1,1,2-tetrafluoroethane in Table 6 and demonstrate the beneficial effect of zinc/iron addition to alumina compared to the addition of any other metal and zinc to alumina.

TABLE 6

EXAMPLE	CATALYST	REACTION TEMPERATURE(°C)			
		350	340	330	320
21	6%Zn/1.5%Fe-Al ₂ O ₃	13.4	9.4	8.5	5.4
22	6%Zn/1.5%Co-Al ₂ O ₃	5.5	4.7	3.2	2.8
23	6%Zn/1.5%Ni-Al ₂ O ₃	5.1	3.4	2.8	1.7
24	6%Zn/1.5%Mn-Al ₂ O ₃	4.7	3.7	2.5	-
25	6%Zn/1.5%Cu-Al ₂ O ₃	3.5	3.0	2.3	-
COMP:	6.6%Zn-Al ₂ O ₃	8.1	6.3		

EXAMPLES 26 and 27.

4.98g of aluminium fluoride, prepared by the reaction of alumina (supplied by Harshaw Ltd) with hydrogen fluoride at 340°C for 48 hours, in the form of granules of size 0.5-1.4mm and having a surface area of 13m²/g was added to an aqueous solution of zinc (II) chloride (0.02g) in distilled water (5ml) and stirred to ensure thorough wetting of the solid by the solution. The mixture was then dried by direct heating and the resultant solid sieved to give particles of size 0.5-1.4mm of a finished catalyst comprising 0.2% w/w zinc on aluminium fluoride. The above procedure was repeated except that a zinc (II) chloride solution of increased concentration was used to give a finished catalyst of 0.5% w/w zinc on aluminium fluoride.

2g of each of these catalysts were tested at atmospheric pressure according to the procedure of examples 1 to 7.

For purposes of comparison the activity of the unpromoted aluminium fluoride from which the promoted aluminium fluoride catalysts were prepared was also tested.

The results of the study are shown as % yields of 1,1,1,2-tetrafluoroethane in Table 7.

10

TABLE 7

EXAMPLE	CATALYST	REACTION TEMPERATURE(°C)		
		340	330	320
26	0.2%Zn-AlF ₃	1.8	1.3	0.9
27	0.5%Zn-AlF ₃	1.9	1.2	0.9
COMP:	AlF ₃	0.1	0.1	0.0

EXAMPLE 28 and 29.

In these examples, the procedure outlined below was carried out using the catalyst prepared in example 7 (example 28) and example 11 (example 29).

0.67g of the catalyst was charged to a 1/4" diameter Inconel reactor tube, dried at 300°C and activated by heating in a stream of hydrogen fluoride at a flow rate of 20ml/minute for one hour. Trichloroethylene and hydrogen fluoride were then fed to the reactor at atmospheric pressure, using a trichloroethylene:hydrogen fluoride ratio of 1:20 and a contact time of 1 second. The activity of the catalyst was monitored at temperatures in the range between

210°C and 250°C and the results are shown as "Initial Activity" in Table 8.

The temperature was then increased to 350°C for a 3 day period of continuous running. After this time, the 5 temperature was lowered to the range 210°C to 250°C and the catalyst activity monitored over this temperature range. The results are shown as "Activity after 3 days" in Table 8. The trichloroethylene and hydrogen fluoride feeds were then turned off and the catalyst was regenerated by heating the 10 catalyst at 350°C in a stream of air at a flow rate of 10ml/minute for 2 hours. After this time, the hydrogen fluoride and trichloroethylene flows were re-established at 20ml/minute and 1ml/minute respectively and the catalyst activity monitored over the temperature range 210°C to 15 250°C. The results are shown as "Activity after Regeneration" in Table 8. All results of the study are presented as % yields of 1-chloro-2,2,2-trifluoroethane in Table 8 and demonstrate the beneficial effect on regeneration of iron addition to zinc promoted catalysts.

TABLE 8.

EXAMPLE	CATALYST	REACTION TEMPERATURE / °C		
5 28	6.6% Zn-Al ₂ O ₃	250	230	210
		20.1	13.7	7.6
		5.1	3.3	1.5
10 15 20	Activity after regeneration	5.7	3.8	2.0
		70.2	48.2	33.4
		32.6	21.1	15.4
	Activity after regeneration	74.3	51.7	35.8

CLAIMS.

- 5 1. A chromium-free fluorination catalyst comprising an activity promoting amount of zinc supported on an alumina, halogenated alumina or aluminium oxyhalide support.
- 10 2. A catalyst as claimed in claim 1 wherein the amount of zinc is from about 0.5% by weight of the catalyst to about 30% by weight of the catalyst.
- 15 3. A catalyst as claimed in claim 2 prepared by impregnation of alumina, halogenated alumina or aluminium oxyhalide with a water-soluble zinc salt and comprising from about 0.5% by weight to about 10% by weight of zinc.
- 20 4. A catalyst as claimed in claim 1 prepared by co-precipitating zinc hydroxide and aluminium hydroxide and thereafter converting the hydroxides to the oxides and in which the amount of zinc is from about 3% by weight to about 30% by weight of the catalyst.
- 25 5. A catalyst as claimed in claim 1 in which the catalyst further comprises one or more metals other than zinc.
- 30 6. A catalyst as claimed in claim 8 in which the metal is selected from the group consisting of nickel, cobalt, manganese, iron and copper.
- 35 7. A catalyst as claimed in claim 6 in which the amount of the metal(s) other than zinc is up to 2.0% by weight of the catalyst.
- 40 8. A catalyst as claimed in claim 9 in which the metal is iron.

9. A catalyst as claimed in claim 8 in which the amount of zinc is at least 3% by weight of the catalyst.

10. A catalyst as claimed in claim 8 or claim 9 in which wt% ratio of zinc to iron is in the range from about 2:1 to about 80:1

11. A catalyst as claimed in claim 3 comprising zinc in an amount at least 3% by weight of the catalyst and which further comprises from about 0.1% to about 2% by weight iron.

12. A catalyst as claimed in claim 4 which further comprises iron and in which the ratio (wt% based on the weight of the catalyst) of zinc to iron is from 16:1 to 2:1.

13. A catalyst as claimed in claim 4 which further comprises iron and in which the ratio (wt% based on the weight of the catalyst) of zinc to iron is from about 16:1 to about 2:1.

14. A process for the production of a fluorinated hydrocarbon comprising reacting a hydrocarbon or a halogenated hydrocarbon with hydrogen fluoride in the vapour phase in the presence of a fluorination catalyst as defined in any one of claims 1 to 13.

15. A process as claimed in claim 14 in which the halogenated hydrocarbon comprises an alkene or alkane having from 1 to 4 carbon atoms and at least 1 chlorine atom.

16. A process as claimed in claim 15 in which the halogenated hydrocarbon is selected from the group consisting of 1-chloro-2,2,2-trifluoroethane, trichloroethylene, 1-chloro-2,2-difluoroethylene and perchloroethylene.

17. A process as claimed in claim 16 which comprises the steps (a) reacting trichloroethylene with hydrogen fluoride whereby to produce 1-chloro-2,2,2-trifluoroethane and (b) reacting 1-chloro-2,2,2-trifluoroethane from step (a) with hydrogen fluoride to produce 1,1,1,2-tetrafluoroethane, in which a catalyst as claimed in any one of claims 1 to 18 is employed in at least one of steps (a) and (b).

18. A process as claimed in claim 17 which comprises the steps of:

(A) contacting a mixture of 1-chloro-2,2,2-trifluoroethane and hydrogen fluoride with a fluorination catalyst at a temperature in the range from about 280°C to about 450°C in a first reaction zone to form a product containing 1,1,1,2-tetrafluoroethane and hydrogen chloride together with unreacted starting materials,

(B) passing product of step A together with trichloroethylene to a second reaction zone containing a fluorination catalyst at a temperature in the range from about 200°C to about 400°C but lower than the temperature in step A to form a product containing 1-chloro-2,2,2-trifluoroethane, 1,1,1,2-tetrafluoroethane, hydrogen chloride and unreacted trichloroethylene and hydrogen fluoride;

(C) treating product of step B to separate hydrogen chloride and 1,1,1,2-tetrafluoroethane from 1-chloro-2,2,2-trifluoroethane, unreacted hydrogen fluoride and unreacted trichloroethylene, and

(D) feeding 1-chloro-2,2,2-trifluoroethane obtained from step C together with hydrogen fluoride to said first reaction zone (step A), in which at least one of the fluorination catalysts employed in step (A) and step (B) is a chromium-free fluorination catalyst as claimed in any one of claims 1 to 18.

19. A process as claimed in any one of claims 14 to 18 in which the catalyst is periodically regenerated by contact with air at a temperature from about 300°C to about 500°C.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 93/00244

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 B01J23/06; B01J23/80; C07C17/20; C07C17/00

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System	Classification Symbols	
Int.Cl. 5	B01J ;	C07C

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP,A,0 333 926 (PENNWALT CORPORATION) 27 September 1989 see claims 1-15; example 2 ----	1-3,5,6, 9,14,15, 19
P,X	WO,A,9 216 482 (E.I. DUPONT DE NEMOURS) 1 October 1992 see claims 1-17 ----	1-3,5,6, 8,9, 14-18
A	DE,A,2 128 341 (MONTECATINI EDISON S.P.A.) 16 December 1971 see claims 1-8 ----	1-3,5-9, 14,15
A	EP,A,0 408 005 (AUSIMONT S.R.L.) 16 January 1991 see claims 1-7 -----	14-18

¹⁰ Special categories of cited documents :

- ^{"A"} document defining the general state of the art which is not considered to be of particular relevance
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- ^{"L"} document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
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^{"T"} later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention^{"X"} document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step^{"Y"} document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.^{"&"} document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

10 MAY 1993

Date of Mailing of this International Search Report

07.06.93

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

CUBAS ALCARAZ J.L.

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

GB 9300244
SA 69760

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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10/05/93

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0333926	27-09-89	US-A-	4827055	02-05-89
		DE-A-	3879178	15-04-93
		JP-A-	1272536	31-10-89
WO-A-9216482	01-10-92	None		
DE-A-2128341	16-12-71	BE-A-	768334	10-12-71
		CA-A-	986494	30-03-76
		FR-A, B	2100741	24-03-72
		GB-A-	1357415	19-06-74
		NL-A-	7107760	14-12-71
		SE-B-	374675	17-03-75
		US-A-	3793229	19-02-74
EP-A-0408005	16-01-91	None		